The Surface Tension of Mixed Liquids

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE IN COLUMBIA UNIVERSITY

BY

MARY AMERMAN GRIGGS, A.B., A.M.

NEW YORK CITY, 1916

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M. A. G.

The Surface Tension of Mixed Liquids

Numerous attempts have been made to discover just what happens when two or more liquids mix to form a homogeneous system, in different proportions. Since, in such cases, neither chemical analysis, nor the application of the phase rule (for there is but one phase present) can give aid, an answer to the question, if obtainable at all, can only be obtained from a study of the changes in the various physical properties brought about by the mixing.

All work based upon the change in a physical property which is caused by the mixing of one liquid with others, depends and must necessarily depend upon the assumption that a general law exists, by aid of which, if no chemical interaction takes place between the constituents, and the individual constituents themselves in the mixture undergo no change of property due to the contact with others, it is possible to calculate from the values of that property for pure constituents, and their amounts present in the system, the magnitude of the property for any one definite mixture. Such a "law of mixtures" has indeed been premised in all work of this sort, but a survey of the literature fails to show any very definite experimental evidence of the general holding of such a law.

The object of this work is the experimental investigation of such a "law of mixtures" with surface tension as the property in question; to find especially how its existence or non-existence can effect the study of abnormal mixtures such as is being undertaken in this laboratory. One possible advantage possessed by these measurements in themselves made as these are by the drop-weight method, is that the surface-tension values so obtained do not require a knowledge of the density of the system as is necessary with results calculated from capillary rise, so that they should be more consistent among themselves and affected by fewer variables than those found by that method.

The simplest form of mixture law is that which involves the

percentages by weight of the constituents, together with their values of the property in question when in the pure state, and of course at the same temperature. Such a law[1] is

$$P_{\text{mixt.}} = l_a P_a + l_b P_b + l_c P_c + \text{etc.}$$

where P is the value of the property in question at any temperature and is the fraction by weight of a constituent in the system, the summation of the terms l being equal to unity. For such a law as this to hold, it is universally conceded that in the mixture there must be no chemical interaction between the constituents, and that the value of the property P of each constituent in the pure state persists in the mixture.

Many investigators, employing various physical properties, after assuming such a mixture law to hold in general, have concluded that variations from it, as illustrated by maxima or minima in the so-called property-composition curves (*i. e.*, those in which the values of the property and of the composition of mixture are employed as the co-ordinates), indicate the presence of chemical compounds, found by the interaction of the

[1] It is difficult to fix the meaning of the terms employed in the mixture law which has been used in the past for the surface tension of a mixture, as no definition was given in the original paper, and various interpretations have been made by subsequent investigators. Thus Rodenbeck (Inaugural Diss. Bonn 1879) formulated the following approximate empirical law for the value of the capillary constant of such mixtures as show no change in volume when the components are mixed:

$$a^2_{\text{mixt.}} = \mu_1 a_1^2 + \mu_1 a^2$$

where μ_1 and μ_2 are called the fractions of the components present (presumably by volume) and a_1^2 and a_2^2 are the capillary constants of the pure constituents.

Volkmann (Ann. Phys. u. Chem., [3] **16**, 20 (1882)), found that a similar law applied to surface tension and gave values in somewhat better accord with experiment:

$$\gamma_{\text{mixt.}} = \mu_1\gamma_1 + \mu_2\gamma_2$$

where μ_1 and μ_2 are stated as being the same as those of Rodenbeck (by volume?). In fact, throughout the literature, no further fixing of μ is indicated and various investigators have assumed it to mean molecular fraction, weight fraction or volume fraction. Thus Whatmough (Z. f. Ph. Ch., **39**, 129 (1902)) uses at times all three of these units, while Worley (J. Ch. Soc., **105**, 267 (1914)) uses volume fractions; both investigators calculate the surface tension.

constituents, while others have also expressed the idea that in part these variations may be due to a mutual breaking of the polymerized molecules previously existing in the pure constituents. Washburn[1] has shown, however, that although these conclusions *may* be justified, we have no certainty that they are.

Denison,[2] on the other hand, has derived theoretically a relation which enables us to differentiate between the effects due to the formation of chemical compounds, and those that are due to a disassociation of one or more of the constituents; and which shows that a further association of these by the mixing would be impossible. His proposed method consists in plotting the *deviation* of the observed value of the property of the mixture from the value of the mixture calculated from the normal mixture law (in place of the value of the property itself) against the composition of the mixture, expressed as a percentage by weight. A maximum point of the curve here indicates the presence of the maximum amount of a chemical compound of a composition identical with that of the mixture exhibiting the maximum, while disassociation of one or more of the constituents is evidenced only by a sagging of the curve.

It will be noted here that there is a decided difference in the meaning of a maximum point in the two types of curve. Thus with the property-composition curve a maximum simply shows at what concentration of mixture *the property itself attains a maximum value*, while in the Denison curve, a maximum represents that concentration at which *the deviation from the mixture law is a maximum*. That the latter means something more than the former is perhaps evidenced by the experimental composition curve, in general, shifts with the temperature, *i. e.*, for the same kind of mixture, the maximum point appears at different concentrations, depending upon the temperature. With the deviation-of-property-composition curve, on the other hand, the maximum deviation from the mixture law is always, according to Denison, found at the same concen-

[1] Tech. Quart., **21**, 360 (1908).

[2] Trans. Faraday Soc., **8**, 20 and 35 (1913).

tration for any one kind of mixture independent of what the temperature may be. A change in temperature here only changes the angle at which the lines, which form the maximum by their junction meet; in other words, the change in temperature simply accentuates or makes less apparent the maximum point.

As far as concerns the Denison method, it will be seen from the above that it is not necessary to premise a mixture law that always gives for normal liquids a calculated value exactly in accord with that observed, for it is not the absolute, but the *relative* deviation of the two values at various concentrations which are employed in abnormal mixtures. So long, then, as a law is found which, assuming the liquids to be normal, gives property values of the mixtures of any system (excepting those which contain extreme proportions of one or more constituents), which differ from the observed values by an approximately constant percentage of error, that law would form a satisfactory basis for the Denison method of treating abnormal mixtures.

EXPERIMENTAL

The surface tensions in this work were determined by the falling drop-weight method, using the Morgan[1] drop-weight apparatus. The usual precautions required in this method were taken. Each drop weight was the means of several results which agreed with one another to within a few hundredths of one per cent. Standard weights and certified thermometers were used.

The mixtures were all made up by weight. In order to prevent change in the composition of the mixtures, the more volatile liquids were added last and the mixtures were always cooled before they were transferred from one vessel to another. Each mixture was always freshly prepared just before being used and a fresh portion was taken for each determination.

The choice of liquids and mixtures and the number of concentrations of the substances in the mixtures were unfortu-

[1] Morgan, J. A. C. S., **37**, 1461 (1915).

nately very materially limited by the present great difficulty in obtaining pure chemicals and by the small quantities of most of them which could be secured. No doubtful liquids were used except when experiment showed that the surface-tension values agreed satisfactorily with those of previous experimenters in this laboratory whose liquids were known to be of the highest purity. This comparison serves as a test both of the purity of the liquids used here and of the accuracy of the results.

The results for single liquids are probably accurate to within a few hundredths of a dyne and for the mixtures to within less than a tenth of a dyne. Attention is called to the fact here, in view of later results, that any change in the composition of a mixture due to the evaporation of one component would mean a raising of a surface tension, for the more volatile substances are in general those which have the lower surface tension.

The tip used gave drop for all the liquids studied which were normal in profile. The standardization was made against benzene at three temperatures and against water at two temperatures. The following equations[1] give the values of the surface tensions of benzene and water that were used in the standardization:

$$\text{Benzene:}\quad \gamma_t = 30.514 - 0.1321t + 0.000082t^2$$
$$\text{Water:}\quad \gamma_t = 75.372 - 0.1547t - 0.00022t^2$$

I. Standardization of Tip.

Liquid.	t.	Ave. wt. (w) 1 drop. (Milligrams.)	Surface tension (γ). (Dynes per centimeter.)	Constant $k = \gamma_t / w_t$.
Benzene.....	25.0°	28.252	27.26	0.9650
Benzene.....	30.0°	27.592	26.63	0.9650
Benzene.....	35.0°	26.926	25.99	0.9653
Water.....	25.0°	74.491	71.87	0.9648
Water.....	30.0°	73.647	71.03	0.9645
			Average,	0.9649

[1] Morgan, Loc. cit.

Therefore the surface tension at any temperature of any liquid, expressed in dynes per centimeter can be found by multiplying its drop weight in milligrams from this tip, at that temperature by this constant. Or for any liquid,

$$\gamma_t = 0.9649 w_t.$$

II. Pure Liquids.

The toluene and chlorbenzene and acetone used in this research, although the purest obtainable, were redistilled and that fraction collected of which the boiling point was constant to within a tenth of a degree. The esters were those which had been especially prepared by Hoffman and Kropff for previous researches.

Toluene.

t.	w.	γ.
15.0°	29.160	28.14
25.0°	27.976	27.00
50.0°	25.028	24.15

From which $\gamma_t = 29.843 - 0.1138t$

Comparison of Surface-Tension Results.[5]

t.	Ramsay & Aston.[1]	Renard & Guye.[2]	Walden & Swinne.[3]	γ calc.
13.1°	...	28.21	...	28.36
15.2°	28.18	...	...	28.11
21.2°	...	...	27.39	27.43
27.1°	...	...	26.73	26.76
29.1°	...	26.33	...	26.53
46.6°	24.60	...	...	24.54
48.0°	...	24.15	...	24.38
59.0°	...	23.10	...	23.13[4]
65.3°	...	...	22.46	22.41[4]
78.4°	20.93	...	...	20.92[4]
79.0°	...	20.92	...	20.85[4]

[1] Z. f. Ph. Ch., 15, 89 (1894).

[2] J. Ch. Ph., 5, 81 (1907).

[3] Z. f. Ph. Ch., 80, 700 (1912).

[4] Extrapolated.

[5] According to the capillary rise work of Richards and Coombs (J. A. C. S., 37, 1656 (1915)), the surface tension of the liquids, benzene, toluene, ethyl alcohol, methyl alcohol, isobutyl alcohol, and ethyl buty-

CHLORBENZENE.

t.	w.	γ.
10.0°	34.544	33.33
25.0°	32.640	31.49
40.0°	30.784	29.70

From which $\gamma_t = 34.535 - 0.1210t$

rate, should be between 3% and 4% larger than the values found by other observers, using the same method, although they find the conventional value for water. The general result of their work, then, is to change the ratio of the surface tension of water to that of the other liquids.

It is interesting to make here a comparison of the relative surface tensions of the above liquids as found by Richards and Coombs with those found by the various investigators working in this laboratory with the drop weight method for surface tension. The values of these ratios which are given in the following table are found from surface-tension values calculated from accurate, experimentally determined temperature equations, to the one temperature, 20°, employed by Richards and Coombs.

SURFACE-TENSION RATIOS.

	R. & C.	From drop-weight method.	
$\frac{\text{Benzene}}{\text{Toluene}}$	1.01225	1.01226	Morgan and Griggs
$\frac{\text{Benzene}}{\text{Ethyl Alcohol}}$	1.2980	1.2960	Morgan and Neidle J. A. C. S., **35**, 1862 (1913)
$\frac{\text{Benzene}}{\text{Methyl Alcohol}}$	1.2790	1.2770	Morgan and Neidle Loc. cit.
$\frac{\text{Benzene}}{\text{Isobutyl Alcohol}}$	1.265	1.263	Morgan and Stone J. A. C. S., **35**, 1510 (1913)

The value of benzene used here in the Richards and Coombs ratio is the mean (28.91) of the two values found by them, using two different capillaries, *viz.*, 28.94 and 28.88 dynes per centimeter. The value used in the other ratios is 27.905, *viz.*, that taken from the conventional average equation for benzene above and used in standardizing the tip. The percentage difference in the values of the ratios by the two methods is never greater than that in the two values for benzene given by Richards and Coombs and is usually less. If the benzene value of Richards and Coombs were used in the standardization of the tip in the drop-weight method, the surface tensions by the two methods would be almost exactly identical. Or the values of the above liquids as reported by the drop-weight method are invariably less than those found by Richards and Coombs, but less by almost identical percentage in all cases. This accentuates the relative accuracy of the surface tensions found from the study of the drop weights from the same tip.

COMPARISON OF SURFACE-TENSION RESULTS.

t.	Renard & Guye.[1]	Ramsay & Aston.[1]	Walden & Swinne.[1]	γ calc.
9.5°	...	33.71	...	33.39
10.7°	33.47	...	...	33.24
18.7°	...	...	32.47	32.27
24.1°	...	...	31.80	31.62
39.0°	29.83	...	...	29.82
41.0°	...	...	29.79	29.57[2]
45.6°	...	29.30	...	29.02[2]
50.8°	28.49	...	...	28.39[2]
52.2°	...	...	28.44	28.22[2]
62.1°	...	...	27.29	27.02[2]

ETHYL PROPIONATE.

t.	w.	γ.
10.0°	25.364	24.47
25.0°	23.588	22.76
40.0°	21.844	21.08

From which $\gamma_t = 25.600 - 0.1132t$

COMPARISON OF SURFACE-TENSION RESULTS.

t.	Morgan & Schwartz.[3] (Recalculated.)	Ramsay & Aston.[1]		γ calc.
10.0°	24.48	24.57	24.67	24.47
33.9°	21.87	...	...	21.76
46.2°	...	20.58	20.62	20.37[2]

METHYL PROPIONATE.

$\gamma_t = 26.436 - 0.1171t.$

t.	w.	γ obs.	γ calc.
15.0°	25.532	24.64	24.68
40.0°	22.488	21.70	21.75

ETHYL FORMATE.[4]

$\gamma_t = 25.327 - 0.1225t.$

t.	w.	γ obs.	γ calc.
15.0°	24.360	23.51	23.49
40.0°	21.248	20.50	20.43

[1] Loc. cit.
[2] Extrapolated.
[3] J. A. C. S., 33, 1041 (1911).
[4] Morgan and Schwartz, Loc. cit.

PROPYL ACETATE.[1]

$\gamma_t = 25.703 - 0.1091t.$

$t.$	$w.$	γ obs.	γ calc.
15.0°	24.956	24.08	24.07
40.0°	22.124	21.35	21.34

METHYL BUTYRATE.[1]

$\gamma_t = 26.331 - 0.1081t.$

$t.$	$w.$	γ obs.	γ calc.
15.0°	25.564	24.67	24.71
40.0°	22.700	21.90	22.01

ETHYL LACTATE.[3]

$\gamma_t = 30.767 - 0.098t + 0.000057t^2.$

$t.$	$w.$	γ obs.	γ calc.
15.0°	30.520	29.45	29.31
40.0°	27.972	26.99	26.94

AMYL HYDROCINNAMATE.

$t.$	$w.$	γ obs.	γ Walden and Swinne.[3]
15.0°	32.500	31.36	32.23
40.0°	30.340	29.28	29.99

ACETONE.[4]

$\gamma_t = 25.172 - 0.1198t.$

$t.$	$w.$	γ obs.	γ calc.
15.0°	24.184	23.34	23.38

Data taken from above experimental results and used to calculate surface-tension values of mixtures according to the law of mixtures.

Liquid.	$t.$	γ
Benzene	10.0°	29.201
Benzene	10.8°	29.097
Benzene	15.0°	28.550
Benzene	40.0°	25.361
Toluene	10.0°	28.705
Toluene	10.8°	28.614
Toluene	15.0°	28.136
Toluene	40.0°	25.291
Chlorbenzene	10.0°	33.325
Chlorbenzene	15.0°	32.720

[1] Morgan and Schwartz, Loc. cit.
[2] Morgan and Kramer, J. A. C. S., 35, 1834 (1913).
[3] Loc. cit.
[4] Morgan and Scarlett, this laboratory (unpublished).

Liquid.	t.	γ.
Chlorbenzene	40.0°	29.695
Ethyl Propionate	10.0°	24.468
Methyl Propionate	15.0°	24.636
Methyl Propionate	40.0°	21.699
Ethyl Formate	15.0°	23.505
Ethyl Formate	40.0°	20.502
Propyl Acetate	15.0°	24.080
Propyl Acetate	40.0°	21.347
Methyl Butyrate	15.0°	24.667
Methyl Butyrate	40.0°	21.903
Ethyl Lactate	15.0°	29.449
Ethyl Lactate	40.0°	26.990
Amyl Hydrocinnamate	15.0°	31.359
Amyl Hydrocinnamate	40.0°	29.275
Acetone	15.0°	23.335

In the following tables all percentage values are given by weight (grams):

III. Mixtures of Two Liquids.

1. Benzene-Toluene:

t.	Benzene.	Toluene.	w.	γ obs.	γ calc.	Deviation.
10.8°	24.98%	75.02%	29.804	28.76	28.74	+0.02
	50.07%	49.93%	29.896	28.85	28.86	—0.01
	75.06%	24.94%	30.064	29.01	28.98	+0.03
40.0°	24.99%	75.01%	26.131	25.21	25.31	—0.10
	47.69%	52.31%	26.136	25.22	25.32	—0.10
	74.98%	25.02%	26.164	25.25	25.34	—0.09

2. Benzene-Ethyl Propionate:

t.	Benzene.	Ethyl Propionate.	w.	γ obs.	γ calc.	Deviation.
10.0°	42.93%	57.07%	27.380	26.42	26.50	—0.08
	54.55%	45.45%	27.924	26.94	27.05	—0.11

3. Benzene-Chlorbenzene:

t.	Benzene.	Chlorbenzene.	w.	γ obs.	γ calc.	Deviation.
10.0°	30.18%	69.82%	32.856	31.70	32.08	—0.38
	46.94%	53.06%	32.128	31.00	31.39	—0.39
	71.19%	28.81%	31.228	30.13	30.39	—0.26
40.0°	30.18%	69.82%	29.004	27.99	28.39	—0.40
	44.54%	55.46%	28.260	27.27	27.77	—0.50
	72.67%	27.33%	27.112	26.16	26.55	—0.39

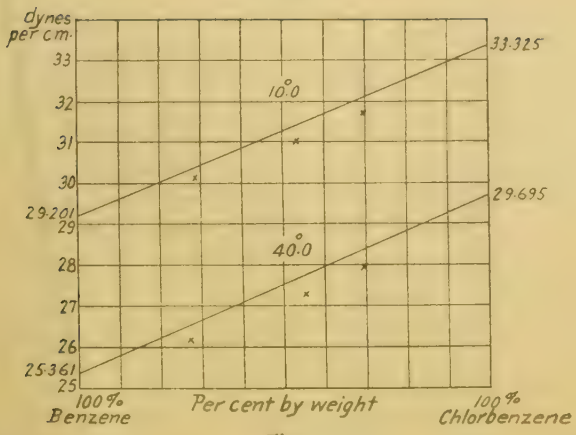

Fig. 1.

4. Benzene-Methyl Butyrate:

t.	Benzene.	Methyl Butyrate.	w.	γ obs.	γ calc.	Deviation.
15.0°	33.62%	66.38%	26.856	25.91	25.97	—0.06
	50.77%	49.23%	27.512	26.55	26.64	—0.09
	77.25%	22.75%	28.680	27.67	27.67	0.00
40.0°	33.62%	66.38%	23.824	22.99	23.07	—0.08
	50.77%	49.23%	24.400	23.54	23.66	—0.12
	77.25%	22.75%	25.412	24.52	24.57	—0.05

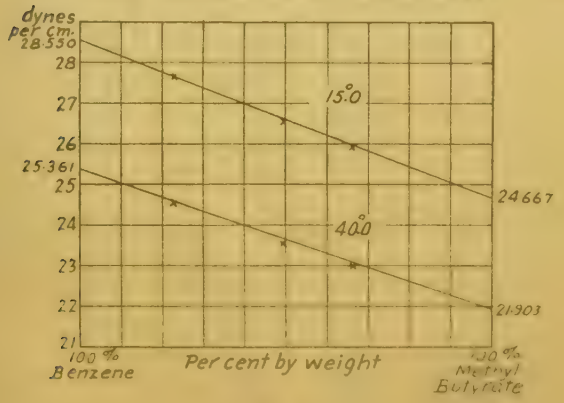

Fig. 2.

5. Benzene-Propyl Acetate:

t.	Benzene.	Propyl Acetate.	*w.*	γ obs.	γ calc.	Deviation.
15.0°	54.97%	45.03%	27.348	26.39	26.54	—0.15
40.0°	54.97%	45.03%	24.248	23.40	23.55	—0.15

6. Benzene-Acetone:

t.	Benzene.	Acetone.	*w.*	γ obs.	γ calc.	Deviation.
15.0°	45.22%	54.78%	26.368	25.44	25.69	—0.25

7. Toluene-Ethyl Propionate:

t.	Toluene.	Ethyl Propionate.	*w.*	γ obs.	γ calc.	Deviation.
10.0°	51.87%	48.13%	27.608	26.64	26.67	—0.03

8. Toluene-Chlorbenzene:

t.	Toluene.	Chlorbenzene.	*w.*	γ obs.	γ calc.	Deviation.
10.0°	21.99%	78.01%	33.172	32.01	32.31	—0.30
	51.08%	48.92%	31.660	30.55	30.97	—0.42
	77.30%	22.70%	30.608	29.53	29.75	—0.22
40.0°	21.99%	78.01%	29.476	28.44	28.73	—0.29
	51.08%	48.92%	28.016	27.03	27.45	—0.42
	77.30%	22.70%	26.964	26.02	26.29	—0.27

9. Toluene-Methyl Propionate:

t.	Toluene.	Methyl Propionate.	*w.*	γ obs.	γ calc.	Deviation.
15.0°	32.67%	67.33%	26.676	25.74	25.78	—0.04
	46.20%	53.80%	27.108	26.16	26.25	—0.09
	74.99%	25.01%	28.196	27.21	27.26	—0.05
40.0°	32.67%	67.33%	23.544	22.72	22.87	—0.15
	46.20%	53.80%	24.072	23.23	23.36	—0.13
	74.99%	25.01%	25.156	24.27	24.39	—0.12

10. Toluene-Ethyl Formate:

t.	Toluene.	Ethyl Formate.	*w.*	γ obs.	γ calc.	Deviation.
15.0°	27.33%	72.67%	25.357	24.47	24.77	—0.30
	51.13%	48.87%	26.312	25.39	25.87	—0.48
	82.02%	17.98%	27.972	26.99	27.30	—0.31
40.0°	27.33%	72.67%	22.272	21.49	21.81	—0.33
	51.13%	48.87%	23.296	22.48	22.95	—0.47
	82.02%	17.98%	25.000	24.12	24.43	—0.31

11. *Chlorbenzene-Acetone:*

t.	Chlorbenzene.	Acetone.	*w.*	γ obs.	γ calc.	Deviation.
15.0°	50.25%	49.75%	27.524	26.56	28.05	—1.49

12. *Chlorbenzene-Ethyl Propionate:*

t.	Chlorbenzene.	Ethyl Propionate.	*w.*	γ obs.	γ calc.	Deviation.
40.0°	50.25%	49.75%	28.948	27.93	28.92	—0.99

13. *Ethyl Lactate-Propyl Acetate:*

t	Ethyl Lactate.	Propyl Acetate.	*w.*	γ obs.	γ calc.	Deviation.
15.0°	28.68%	71.32%	26.108	25.19	25.62	—0.43
	51.59%	48.41%	27.140	26.19	26.85	—0.66
	78.83%	21.17%	28.788	27.78	28.31	—0.53
40.0°	28.68%	71.32%	23.300	22.48	22.97	—0.49
	51.59%	48.41%	24.400	23.54	24.26	—0.72
	78.83%	21.17%	26.124	25.21	25.80	—0.59

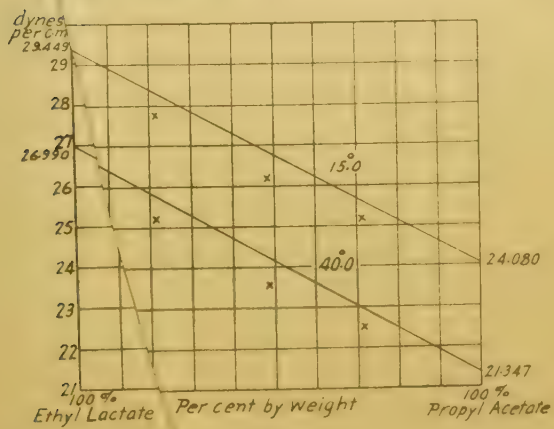

Fig. 3.

14. *Chlorbenzene-Methyl Butyrate:*

t.	Chlorbenzene.	Methyl Butyrate.	*w.*	γ obs.	γ calc.	Deviation.
15.0°	53.51%	46.49%	29.156	28.13	28.98	—0.85
40.0°	53.51%	46.49%	26.204	25.28	26.07	—0.79

15. Amyl Hydrocinnamate-Methyl Propionate:

t.	A. H.	M. P.	*w.*	γ obs.	γ calc.	Deviation
15.0°	51.52%	48.48%	28.244	27.25	28.10	—0.85
40.0°	51.52%	48.48%	25.390	24.50	25.60	—1.10

16. Acetone-Propyl Acetate:

t.	Acetone.	Propyl Acetate.	*w.*	γ obs.	γ calc.	Deviaton.
15.0°	49.70%	50.30%	24.484	23.63	23.71	—0.08

IV. Mixtures of Three Liquids.

17. Benzene-Toluene-Ethyl Propionate:

t.	Benzene.	Toluene.	Ethyl Propionate.	*w.*	γ obs.	γ calc.	Deviation.
10.0°	34.29%	33.43%	32.28%	28.480	27.48	27.51	—0.03

18. Benzene-Toluene-Chlorbenzene:

t.	Benzene.	Toluene.	Chlorbenzene.	*w.*	γ obs.	γ calc.	Deviation.
10.0°	31.34%	32.78%	35.89%	31.208	30.11	30.52	—0.41
40.0°	30.36%	33.66%	35.97%	27.420	26.46	26.89	—0.43

19. Benzene-Toluene-Methyl Propionate:

t.	Benzene.	Toluene.	Methyl Propionate.	*w.*	γ obs.	γ calc.	Deviation.
15.0°	33.07%	33.68%	33.25%	28.012	27.03	27.11	—0.08
40.0°	33.07%	33.68%	33.25%	24.830	23.96	24.12	—0.16

20. Benzene-Toluene-Acetone:

t.	Benzene.	Toluene.	Acetone.	*w.*	γ obs.	γ calc.	Deviation.
15.0°	30.99%	32.87%	36.15%	27.192	26.24	26.53	—0.29

V. Mixtures of Four Liquids.

21. Benzene-Toluene-Ethyl Propionate-Chlorbenzene:

t.	Benzene.	Toluene.	E. P.	Chlor-benzene.	*w.*	γ obs.	γ calc.	Devia-tion.
10.0°	23.18%	27.62%	18.45%	30.74%	30.028	28.97	29.46	—0.49

22. Benzene-Toluene-Methyl Propionate-Ethyl Lactate:

t.	Benzene.	Toluene.	M. P.	E. L.	*w.*	γ obs.	γ calc.	Deviation.
15.0°	24.60%	24.09%	27.74%	23.58%	28.34	27.33	27.58	—0.25
40.0°	24.60%	24.09%	27.74%	23.58%	25.04	24.32	24.72	—0.40

23. Benzene-Toluene-Methyl Butyrate-Propyl Acetate:

t.	Benzene.	Toluene.	M. B.	P. A.	*w.*	γ obs.	γ calc.	Deviation.
15.0°	23.57%	26.28%	24.56%	25.59%	7.232	26.28	26.34	—0.06
40.0°	23.57%	26.28%	24.56%	25.59%	24.184	23.34	23.47	—0.13

VI. Mixtures of Five Liquids.

24 *Benzene-Toluene-Methyl Butyrate-Propyl Acetate-Methyl Propionate:*

t.	Benzene.	Toluene.	M. B.	P. A.	M. P.	*w.*	γ obs.	γ calc.	Deviation.
15.0°	17.61%	20.50%	20.17%	21.01%	20.72%	26.784	25.84	25.94	—0.10
40.0°	17.61%	20.50%	20.17%	21.01%	20.72%	23.716	22.88	23.05	—0.17

DISCUSSION OF RESULTS

Of the twenty-four differently constituted mixtures studied in this research, almost all being considered in several proportions and at two temperatures (*viz.*: 16 of two constituents, 4 of three, 3 of four, and 1 of five) the mixture law, depending upon the relative weights in grams of the constituents may *be said to hold rigidly*, if we accept 0.1 dyne per centimeter as a plausible experimental error, *in ten cases* (*viz.*: 6 mixtures of two constituents, 2 of three, 1 of four, and 1 of five). Figure 2 shows graphically the experimental values obtained for one such system. A similar result is also obtainable from the drop weight measurements of Morgan and Thomssen[1] of an equal weight mixture of another system, benzene and carbon tetrachloride, where the deviation of the calculated from the experimental value is but 0.03 dyne per centimeter, a fact that is confirmed for this system is a different relative proportion by the work of Ramsay and Aston.[2] The latter investigators find further that a similar following of this law is exhibited by two mixtures in different proportions of toluol and piperidine.

For the other fourteen systems studied above the calculated result is found to deviate from that observed, by amounts varying from 0.15 to 1.5 dynes per centimeter, *the observed result being consistently and invariably smaller* than that calculated.

Further, the deviations here are always greater at 40° than those at 10°. Figure 1 shows a system where the deviations are small, and Figure 2 one where they are large.

Perhaps the most important experimental result obtained in this work, in connection with the deviation, when it exists,

[1] J. A. C. S., 33, 667 (1911).

[2] Loc. cit.

being invariably in the same direction, is the fact that the maximum deviation is invariably exhibited by those mixtures which contain approximately equal parts by weight of the constituents. So consistent was this result that those mixtures which for one reason or another could not be studied in more than one proportion by weight, were invariably measured on an equal weight basis, since plainly that mixture would show the maximum possible deviation of such a system, and would present the worst possible condition for the holding of the mixture law.

It is possible that such deviations as those found above may be dependent upon two factors, one of which is certainly of great importance, while the other may perhaps ultimately be found to merge completely and invariably into the other. The latter factor, of doubtful meaning, is the magnitude of the difference existing between the surface-tension values of the constituents themselves, when in the pure state—the former being the specific chemical nature of the substances. That the difference in magnitude of the constituents' surface tensions may have no effect in some cases at least, and the specific nature a large effect, is shown by contrasting the mixtures of toluene and ethyl propionate on the one hand, where the constituents differ in surface tension by 4.24 dynes per centimeter, and yet the deviation of the observed from the calculated values of the mixture is but 0.03 dyne per centimeter, and those of toluene and ethyl formate, on the other, which while exhibiting a difference of 4.63 dynes per centimeter themselves, lead to a deviation of the mixture of 0.48 dyne per centimeter.

This naturally points to a decided difference in effect, when mixed with toluene, of ethyl propionate and ethyl formate, which can only be due to a difference in the specific nature of the two. Further, *all* mixtures containing chlorbenzene invariably show large deviations from the mixture law, while those containing benzene show none at all, or at worst much smaller ones, although the surface tensions at 10° are, respectively, 33.33 and 29.20 dynes per centimeter. This result for chlorbenzene mixtures is confirmed by the work

of Ramsay and Aston[1] who find the mixture of chlorbenzene and ethylene dibromide gives large variations from the calculated values the deviation in this case, contrary to the one above, seeming to decrease at a higher temperature. In the same way chloroform and carbon disulphide mixtures as found by them give large deviations, but whether this is due to the chloroform or the carbon disulphide, or to both, cannot be stated, as no other mixtures of either were studied.

It will be noted from the tables above that in all binary mixtures the maximum deviation is at a concentration of approximately equal weights of the constituents, and except at extreme relative concentration of the constituents, is roughly constant. As was mentioned above, this would not affect the result obtained from the deviation of property-composition curves nearly as much as it would affect the comparison of the calculated and observed values of the mixture for it is the relative deviation at various dilutions employed in this curve and the difference in the deviations at various concentrations are very much smaller than the deviations from the law at any one concentration. In this case, however, this conclusion could only be drawn for mixtures which are not extreme (relatively) in concentration; for a very small amount of the one liquid could not affect the value of the mixture so considerably and consequently would cause the law to hold to a better degree.

The study of mixtures containing more than two constituents, makes evident the fact that the law still holds most satisfactorily in certain cases. The deviations, when they are present, are never additive, but rather of the same order as the deviations of the pairs of constituents of which they could be made. Thus the deviation of a benzene-methyl butyrate-toluene-propyl acetate mixture is of the order of the deviation of the benzene-methyl butyrate or the benzene-propyl acetate or the benzene-toluene mixtures, and is not equal to the summation of their deviations.

Since we cannot prove by any known direct method that the liquids used in the mixtures studied in this research either

[1] Loc. cit.

react chemically with one another in the mixture, fail to react, or whether the constituents are really associated when pure or not, or whether such a possible state of association is changed, or not on mixing, we are free to make two assumptions as to the holding of a mixture law, and to choose the more plausible and consistent to serve as a temporary guiding principle which may aid in obtaining a definite answer to the question ultimately.

I. If *all* these mixtures studied are really free from chemical reaction between the constituents, and no change of the individual constituents of any sort results from the mixing—then the mixture law in the above form is plainly a failure, capable of errors which are certainly beyond the experimental errors of even the roughest of methods. It could still be used as the basis for a Denison method, however, even in this form, for the degree of error (*i. e.*, the deviation with the total deviation) in which form it is applied there is much smaller than the absolute error of the law itself.

II. If, on the other hand, we assume in some of the above mixtures that slight changes are possible, of the nature perhaps, of a change in the property of the constituents themselves due to the mixing, rather than the formation of a new compound, then the mixture law can be considered as a rigid law in those cases, in which no changes of this sort occur.

The experimental results here show that in ten cases the law holds rigidly, while in the other 14 there is invariably a negative deviation of the experimental from the calculated value, with a maximum deviation invariably at an equal weight (in grams) concentration of mixture. Further than this, certain definite liquids are found to invariably affect their mixtures with every other liquid in such a way as to lead to an abnormal result similar to the above.

As no one liquid could conceivably be assumed to interact chemically with *all* others, and as chemical interaction, if it takes place, could not possibly lead in all cases and invariably to the greatest amount of a compound formed at an *equal-weight* (in grams) mixture of the constituents, it would seem

that a chemical interaction of the constituents as the cause of the deviation would be a thing very far indeed from the facts.

This conclusion would leave only an effect of one liquid upon the property of the other, or a similar mutual effect of the constituents upon one another, as a possible explanation of the observed deviation. That explanation, however, would seem to lead directly and exactly to such results as those above. For if $P_{mixt.}$ in the equation $P_{mixt.} = l_a P_a + l_b P_b$, is to vary to a maximum, through, for example, a change in the value of P_b, as caused by the presence of the other unchanged liquid, and, naturally, proportional to the amount of this, it is clear that the maximum effect on P_{mixt} must be due to a maximum change in the whole term $l_b P_b$ and not in P_b alone. And since to produce this, l_b would have to be as large as possible, and P_b would have to be affected as much as possible, (*i. e.*, l_a would have to be as large as possible), it is clear that the maximum effect on P_{mixt} (*i. e.*, on $l_b P_b$) would be observed at a concentration of 50% of each of the two constituents. For the greatest change in the term $l_b P_b$ must necessarily be brought about, and only then, when the maximum possible amount of liquid is affected to the greatest extent possible, *i. e.*, by the greatest amount of the other; and since $l_a + l_b = 1$ by definition, l_a in the mixture must be equal to l_b and each equal to 0.5.

Since the highest temperatures indicate increased abnormality in result over those at the lower, although the maximum point remains at the 50% concentration, the effect of one liquid upon the property of another, or the mutual effect of the liquids upon one another, must increase with increased temperature.

This reasoning it is thought makes Supposition II the one which is to be regarded as probably true, at least with regard to such mixtures as have been studied in this work.

With respect to other forms of the mixture law applied to the above results, it must be noted here that using either the volume per cent or the molar per cent, in place of the weight per cent fails to lead to as satisfactory a general result as that given above. As no theoretical reasons exist for the selection

of either of these over the latter for the property of surface tension, although, for example, the molar fraction might be necessary for some properties, as volume of a gaseous mixture, the matter need not be discussed further here, although all values have been calculated. It is of interest, however, to state that using molar fraction form, the values of the chlorbenzene mixtures, abnormal above, become normal and some of the normal mixtures become abnormal. In both these forms of law, the deviations are found to be irregular, sometimes negative, sometimes positive. This would seem to show that surface tension is not entirely a molecular property.

Ramsay and Aston[1] and Kremann and Meingast[2] have studied the additive property of the function $\gamma(m/d)^{2/3}$ in place of γ, with some success. It must be confessed, however, that this relationship complicates the question somewhat, in that a change of density on mixing could conceivably counteract and render invisible a real effect on the surface tension. It would seem that something of this sort often occurs, for Kremann and Meingast find the value of $\gamma(m/d)^{2/3}$ for the mixture to be additive for 22 out of the 24 liquids studied. For purposes of segregating groups of liquids according to their effect when mixed, the relationship can hardly be said to be as useful as the one we have used.

SUMMARY

The results obtained in this research may be very briefly summarized as follows:

I. From the surface tensions, by the drop-weight method, of twenty-four homogeneous mixtures in various proportions and at two temperatures, it was found that 10 follow rigidly the law of mixtures in the form $P_{mixt.} = l_a P_a + l_b P_b +$ etc. (where the summation of the relative weights l_a and l_b is equal to unity). Of these mixtures, 6 were of two constituents, 2 of three, 1 of four and 1 of five.

II. Whenever variations appear (the other 14 mixtures) the observed value is invariably less than that calculated from the law. These deviations increase in magnitude with in-

[1] Loc. cit.

[2] Monatshefte. f. Chem., 35, 1323 (1914).

creased temperatures, and are always at a maximum, at both temperatures, for that mixture which contains equal weights of the constituents.

III. Although the deviations might be due to the magnitude of the difference in the surface-tension values of the constituents when pure, the effect is probably negligible and merges into the more important factor—the nature of the constituent. An example of this latter is chlorbenzene which renders every mixture, in which it is, abnormal. The deviation of a complex mixture is not a summation of the deviations of the pairs of liquids of which it could be made, but is of the same order as these.

IV. It is shown that chemical interaction for binary mixtures could not be the cause of the maximum deviation invariably found at a composition mixture of 50% by weight of the two constituents whereas this behavior is shown to be exactly that which might be expected if the one liquid by its simple presence influenced the property of the other (or each affected the other), and the conclusion is consequently drawn that the mixture law is a rigid law, provided no chemical interaction takes place between the constituents, and neither liquid influences the property of the other. The effect of this latter action is invariably to produce the maximum deviation at 50% mixture by weight of the two constituents.

VITA.

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